ELECTRODEOXIDATION OF SOLID Fe_2O_3 IN MOLTEN $CaCl_2$ TO PRODUCE IRON

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ABSTRACT

The industrial production of iron and steel contributes to a significant share of the global CO_2 *emissions. Electrochemical methods using an inert oxygen evolving anode can eliminate the* CO_2 *formation. The FFC Cambridge process approach was tried out for the reduction of hematite to produce iron at 915°C. The electrolyte consisted of pure molten* $CaCl_2$ *containing 0.5 mol% CaO. Different anodes were tested. Graphite anodes were found to halt the reduction of the inner parts of the cathode pellets. Also large amounts of carbon were found in the cathode product in these experiments. Nickel ferrite cermet with intergranular nickel and copper was tried as an inert oxygen evolving anode material. These anodes showed promising behaviour and also made the cathode pellet more active with respect to electroreduction. Iron was formed at the cathode during the process.*

INTRODUCTION

A new method for producing titanium by molten salt electrolysis was published [1], and later this process has been named the FFC Cambridge process after the authors Fray, Farthing, and Chen of the University of Cambridge, United Kingdom (*FFC stands for what?*). The basis of the process is to contact a solid metal oxide to a cathode placed in molten $CaCl_2$. Upon passage of current the metal is reduced without going into solution while the oxide dissolves in the electrolyte as oxygen ions. The anode process will give CO_2 on a carbon anode, or more preferably oxygen gas using an inert anode. Molten calcium chloride is used as electrolyte because of the very high solubility of CaO [2]. In principle any metal oxide can be electrodecomposed in this way provided that the metal is nobler than calcium. The role of calcium is not fully understood, but the formation of dissolved calcium may aid in the process of reducing the metal ions. The process has successfully been applied to produce several metals, in particular titanium, tantalum, chromium and silicon. All these metals are less noble than iron, which should make the FFC Cambridge iron production feasible.

Oxygen is soluble in solid titanium metal [3] and removing the residual oxygen from the metal phase is the slowest and least efficient part of the FFC Cambridge process. As oxygen does not dissolve in the solid metal iron phase, removal of residual oxygen is not considered to halt current efficiency in the same manner for iron as it does for the titanium production route.

In previous work on the FFC Cambridge process mainly graphite anodes and only quasi reference electrodes have been used. In the present work a candidate nickel ferrite cermet anode was investigated along with graphite anodes. Also a proper reference electrode based on silver/silver chloride was taken into use.

Recently Kilby *et al.* tested out a tin oxide based anode material at 900 °C for the FFC Cambridge titanium process while measuring the exhaust gas with respect to oxygen content [4]. It was found that oxygen was produced at a rate similar to the production rate of titanium metal.

The motivation of this work is due to an initiative by the steel industry in Europe to start a research program to develop new processes for producing iron and steel with low emissions of CO_2. ULCOS is short for Ultra Low CO_2 Steel making. One possibility is to produce iron by electrolysis.

Possible reactions that can take place in the given electrolyte are shown in Figure 1. One can see that CO_2 will be reduced to carbon at approximately the same potentials as the last reduction step of iron oxide. Furthermore, the cathodic overpotentials for the iron oxide reduction can be more than one volt without producing calcium metal at unit activity.

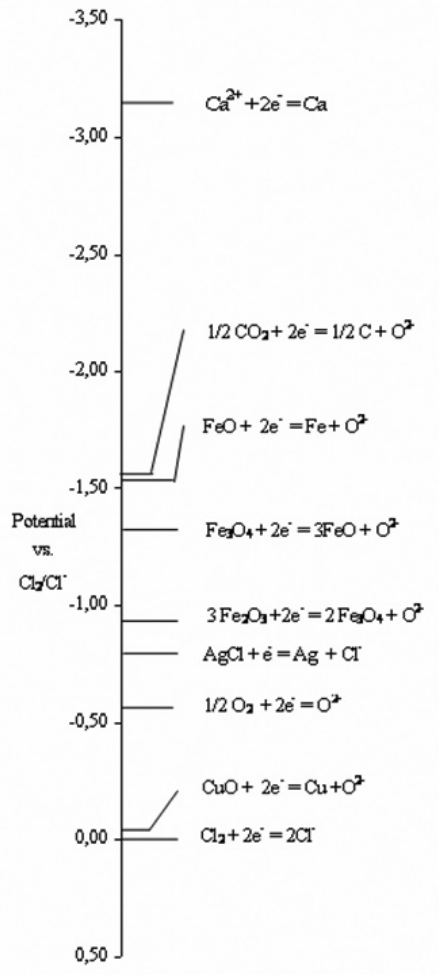

Figure 1: Standard electrode potentials at 800°C for reduction reactions in the given system referred to the standard chlorine electrode [5, 6, 7]

METHODOLOGY

All experiments were carried out in a closed reactor continuously purged with argon. In the bottom of the reactor, the electrolysis cell was placed. A sketch of the cell is given in Figure 2. The thermal shield had five holes, 13 mm diameter each, in the top. The purpose of this shield was to prevent loss of electrolyte due to convection and loss of heat due to radiation. The temperature range was from 810-920ºC. The temperature was controlled by a Eurotherm 2408 control unit. The electrolyte consisted of pure $CaCl_2$ containing 0.5 mol% CaO. The $CaCl_2$ was dried for 48 h at 180ºC and below 1 kPa, in order to remove residual water.

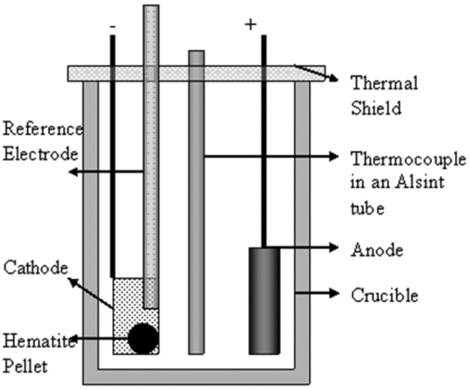

Figure 2: The design of the cell and its components connected to the power-supply

The reference electrode consisted of a sealed mullite ($3Al_2O_3.2SiO_2$) tube (450 mm), filled with 0.2 g NaCl, 0.4 g $CaCl_2$, 0.06 g AgCl in the bottom, and a silver wire (1.0 mm diameter) going from the bottom and out of the sealed top.

The cathode consisted of a custom made ss316 steel basket (20 mm od, 16 mm id, 20 mm oh, 18 mm ih) connected with an ss316L welding rod (3 mm diameter). The cathode contained hematite pellets, the raw material for the process. The pellets were highly porous and not sintered at a high temperature, as this is not required for the blast furnace process.

The anodes were either graphite (HKO grade) or custom made nickel ferrite cermet containing excess nickel and copper.

The current was measured by using four parallel coupled resistors (each 10 ohm and 50 watt) over which the electric potential was logged. Hence currents up to 8.94 A could be measured. All potentials were measured with an Agilent Acquisition Switch Unit 34970A.

XRD was performed with a Philips X'Pert PW3020 (theta/2theta, 2 motors) x-ray difractometer.

The ICP analyses were performed with a Varian Liberty AX sequential ICP-AES spectrophotometer.

The SEM investigations were performed with JEOL JSM-5500 LV scanning electron microscope, and the EDS measurements were performed with EDS, INCA x-sight 6587, OXFORD INSTRUMENTS.

Oxygen contents were measured with an ELTRA ONH–2000 Oxygen/Nitrogen/ Hydrogen analyser.

The obtained samples were cleansed in boiling water. Boiling water has high solubility of salts and low solubility of oxygen compared to cold water. Hence, residual $CaCl_2$ was effectively removed and the reaction between iron and oxygen was reduced.

RESULTS AND DISCUSSION

The FFC Cambridge Standard Example

The FFC Cambridge process is usually run by a two electrode setup, where the experiment is run at constant cell potential to the electrode holders. The experiments in this report are either run at constant current or at fixed constant cathode potential vs the reference electrode. Figure 4 shows typical time and current beaviour for a lab scale FFC Cambridge electrolysis setup, here at 815°C controlled by cathode potential at -2.0 V vs. the reference electrode. In the beginning of the electrolysis time, presumably the hematite, Fe_2O_3, is reduced to magnetite, Fe_3O_4, with available electrode overpotential of approximately 1.1 V. This can be seen from Figure 1. The current is at its peak, unstable and unpredictable. The second reduction step is then assumed to be the reduction of magnetite to wustite, FeO, with a theoretical overpotential of approximately 0.6 V. The last reduction step is then wustite to metal iron, with an over potential of approximately 0.5 V. During the last two reduction steps the current drops until the available iron oxides are reduced and the cell reaches its background current. This background current represents loss in current efficiency. Parallel along with the reduction of iron dissolved carbon oxides will be reduced at the cathode with available overpotential of approximately 0.4 V. These conditions are theoretical electrochemical cathode considerations and will be discussed further.

The Electrolysis Cell

By visual inspections of the cell, after cooling to room temperature, graphite particles were found to float on the top of the cell, even when the electrolysis were not carried out (mostly due to break down of electrodes and connectors). The part of the graphite anode being above the electrolyte and below the thermal shield was found to be the most worn region of the anode and assumed to be the source of the carbon dust. Hence a diaphragm was applied to see if possible a current leakage through this top layer could be removed. The diaphragm consisted of a porous cylindrical alumina crucible, with the carbon anode inside it. The porous crucible used in this work had a pore size less than 30 microns with 5 mm thick wall. Figure 3 shows the logged current of two runs with the diaphragm and two without. The experiments were carried out at 815°C with constant cathode potential at -2.0 V vs the reference electrode. The pellets weighed 3.3 ± 0.2 g. During these four experiments, it was found that the current on average was lowered by approximately 0.2 A when taking the diaphragm into use. We now distinguish between electronic conductivity in the carbon layer on top of the electrolyte and the ionic conductivity in the electrolyte. Hence, by removing the electronic conduction in the carbon floating on top of the electrolyte, the electrochemical current in the electrolyte is recorded. There was no significant effect on the current by increasing the temperature up to 915°C. There was no chance of electrical contact between the diaphragm and the cathode, and thus it is not likely that the alumina would be reduced or short-circuiting of the cell.

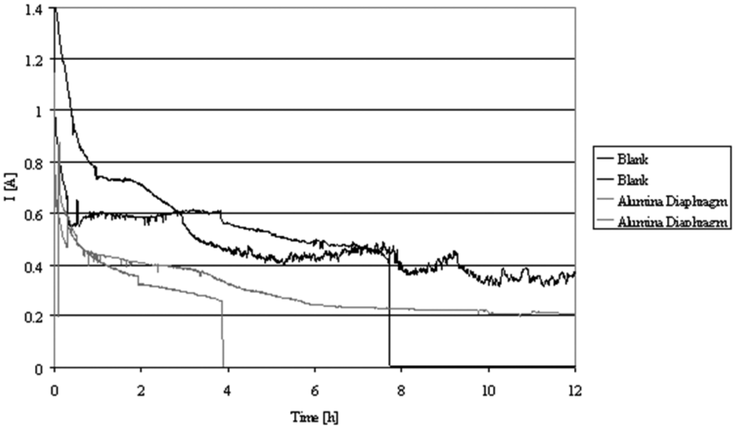

Figure 3: Current vs. time of reduction of hematite pellets (3.3 ± 0.05 G) with a diaphragm around the anode (Grey) and without (Black) in $CaCl_2$ Containing 0.5 Mol% CaO at 815°C

As mentioned, carbon present in the electrolyte as dissolved carbon dioxide, CO_2 (diss) has an electrode reduction potential close the last reduction step of iron oxide. In terms of energy, the most favourable anode oxidation reaction in the presence of oxygen ions is carbon oxidising to CO_2. In the electrolyte composition used in the presented experiments, CO_2 is assumed to exist as calcium carbonate, $CaCO_3$ (diss). [8] determined $CO_3^{2-}$by voltammetry in the $CaCl_2$-CaO system [9]. Either the dissolved carbonate will electrodeposit directly onto the cathode or it will react with dissolved calcium metal, Ca (diss). Figure 4 shows how the current depends on the cathode potential when using a graphite anode. The data were recorded at steady state conditions between 3.5 h and 4.5 h. When applying cathode potentials below -2.8 V_{Cl2/Cl^-}, the current values increased more than the linear relation. When applying potentials below -2 V vs. reference electrode to the cell, the activity of calcium at the cathode will start to become significantly. From a thermodynamic point of view, calcium activities above 10^{-4} are reasonable. Two effects may occur in this potential region. First the electrolyte starts to give electronic conductivity. This is found to be due to dissolved calcium, Ca (diss) [9]. Calcium dissolves as a complex, were an ionic calcium species reacts with a calcium species forming to calcium ions with a charge of one each, see Equation 1.

$$Ca_{diss} + Ca^{2+}_{(diss)} = Ca^{2+}_{2(diss)} \qquad (1)$$

However, for electronic conductivity to occur in the electrolyte, the dissolved calcium must be present throughout the electrolyte. Hence, the second alternative is suggested. Calcium diffuses from the cathode into the electrolyte were dissolved carbonate and dissolved calcium reacts to form carbon and calcium oxide, see Equation 2a and b. The way these species are expected to exist as components in the electrolyte is described in Equation 3.

$$\frac{1}{2} CO_2 + 2\,e^- = \frac{1}{2} C + 2O^{2-} \qquad (2a)$$

$$\frac{1}{2} CO^{2-}_{3(diss)} + 2e^- = C_{(s)} + 3O^{2-}_{(diss)} \qquad (2b)$$

$$4CaCl_{(diss)} + CaCO_{3(diss)} = C_{(s)} + 3\,CaO_{(diss)} + 2\,CaCl_{2(l)} \qquad (3)$$

Reaction (3) is hence suggested to occur at the cathode and thus contribute significantly to the loss in current efficiency.

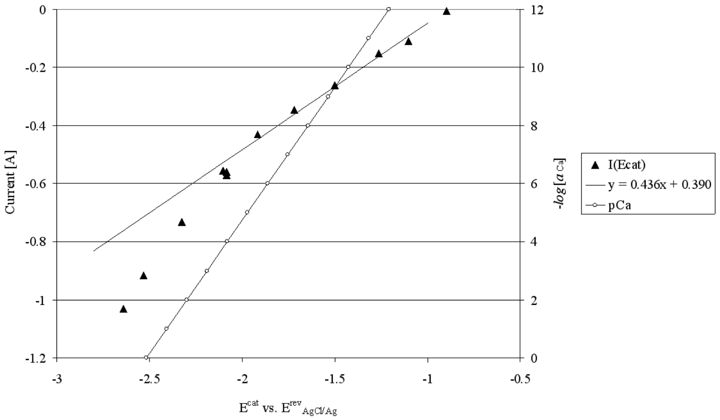

Figure 4: Steady state current (Left Y-Axis) recorded at the end of the process vs. cathode potential (AgCl/Ag Reference) in Molten $CaCl_2$ containing 0.5 Mol% CaO at 815 °C. Calculated activities of calcium metal (Right Y-Axis) vs. standard potential at 827 °C

The Cathode

As the traditional way of running the FFC-process is by the use of graphite electrodes, this study gives a unique opportunity to see how carbon oxide in the electrolyte affects the cathode. We have discussed the likely possibility for carbon to be reduced at the cathode. This was also found to happen. By running the cathode continuously at -2.8 $V_{Cl2/Cl-}$ for twelve hours, as much as 20 wt% carbon, equal to 54 mol% carbon, was found in the cathode product. These levels were determined by leaching some of the cathode product in approximately 1.0 M HNO_3 and filter it. Carbon was assumed to be the only species that does not dissolve in acidic solution, as iron carbide was not found by XRD investigations.

The reduction process activity of the hematite pellet at the cathode was found to be halted by precipitation of carbon. When using graphite anodes, only the outer layer of the hematite pellets was found to be fully converted during every experiment. Carbon seems to deposit at the cathode pellet and thus close the pores necessary for the electrolyte to conduct oxygen ions into the electrolyte. Oxygen species in the electrolyte are assumed to occur as calcium oxide, CaO (diss) [2]. As already mentioned, the hematite pellets used for experiments in this paper are of the kind which is also used in mass ovens and therefore highly porous. EDS-investigation of the pellets showed that the core of the pellets consisted of a solid mixture of iron, calcium and oxygen and the outer part consisted of iron and iron oxide. The reason why iron oxide occurs in the areas which are converted is assumed to be related to a back reaction during washing. Even though the oxygen dissolved in water was removed by boiling, iron will react with water to form iron oxide and hydrogen as iron is a reactive material in water. Iron oxide will also occur if the material is not fully converted.

Previous work on the titanium FFC Cambridge process has revealed that the outer part of the titanium oxide pellet is converted before the inner part [10]. This is assumed to be because titanium oxide is not conductive and electronic conductivity in the outer spherical must be obtained before the inner part can be reduced. However, in this work large amounts of magnetite, Fe_3O_4, were found in the core of the pellet, by XRD investigation. Magnetite is conductive and the inner part was not reduced in all experiments even though. This result, suggests that electronic conductivity in the core of the cathode pellet is redundant in the absence of ionic conductivity, and that the use of carbon anodes may be the reason. It further suggests that all the hematite is reduced to magnetite before carbon blocks the reduction reaction in the core of the pellet.

Introducing the nickel ferrite cermet anodes activated the hematite pellet in comparison to the use of graphite anodes. The iron oxide particles in the pellet slowly dispersed into the electrolyte and were furthermore reduced at the cathode basket forming an iron sponge. This sponge covered all the surface of the cathode basket. The dispersion effect occurs due to the hematite pellets not being sintered properly or being exposed to carbon reduction precipitation. The iron sponge around the cathode basket was also observed to a very limited degree when using graphite anodes. Hence, it is again emphasized that carbon co-reduces at the cathode pellet, and thus binds the pellet together. Some of the dispersed hematite was also found to stabilize as magnetite at the anode.

Inert Anode Behaviour

The major problem which was expected for the nickel ferrite cermet anodes was loss of copper into the electrolyte. This is not a problem in itself, but tin and copper represents a severe problem in steel refining because copper and tin are extremely hard to remove by slag processes [11]. Table 1 shows results of electrolysis run for 12 hours. Two anodes were used and one of them was run twice. As a tentative conclusion, copper dissolves higher at 25 mA cm^{-2} compared to 50 mA cm^{-2}. Furthermore, copper dissolves significantly less during the second run. As can be seen, copper content was lowered from 100 000 ppm down to 1000 ppm. The anodes were both pre-electrolysed for four hours at 25 mA cm^{-2}. This suggests that the anode should be pre-electrolysed for a longer time and that the current density during the electrolysis should be run at 50 mA cm^{-2} rather than 25 mA cm^{-2}, or perhaps even higher. It also suggests that the copper should be replaced by another intergranular metal. For metals different from iron, traces of copper might not harm the cathode product and this issue will not be a problem. As mentioned, magnetite was stabilized at the anode surface. As magnetite is conductive and stable, this oxide should be further investigated as an oxygen evolving material. The main advantage for this is that magnetite is cheap and that loss of anode material does not contaminate the product in the case of making iron.

The oxygen contents in the cathode product shown in Table 1 change little with the Current Ratio and Current Efficiency. This suggests that either one can not obtain lower oxygen levels or the oxygen content is due to back reaction when cleaning in water. Current Efficiency is the relation between charge passed through the cell and the material gathered after cleansing times hundred. Current Ratio is the relation between charge passed through the cell and the iron oxide applied to the cell before starting the run times hundred. As some of the material disappear during the process and other elements, such as copper, might be added to the cathode product the Current Efficiency gives different values from the Current Ratio. As an example, anode I run I gives a current ratio of 124.4%. Comparing the oxygen levels of all the runs with this run one can see that it is not necessary to apply all 100% of the theoretical charge. However, the current efficiency reveals problems on gathering the entire product on a lab scale. Evaluation of the FFC Cambridge process by the charged applied to the cell is hence difficult. These problems are only discussed to a very limited extent for the FFC Cambridge process.

Table 1: Overview of the properties given for the cathode and the anode, and elemental analysis of the cathode product

Anode Conditions		**Cathode Conditions**				**Cathode Product**		
	i [mA/cm^2]	**m Fe_2O_3 [g]**	**Current Efficiency (%)**	**Current Ratio (%)**	**Ca [wt%]**	**Al [wt%]**	**Cu [wt%]**	**O [wt%]**
Anode I Run I	25	3.37	87.0	124.4	1.1	0.13	10.1	14.0
Anode I Run II	50	3.21	23.5	15.6	2.7	0.11	0.12	12.2
Anode II Run I	50	3.16	45.3	41.9	3.4	0.04	1.1	13.1

In refining of steel lime and aluminium is added to molten steel. Aluminium is added to reduce residual iron oxide, see Equation 4 and the lime is added to form a slag which can adsorb the formed alumina. It is suggested that 1.5-3 g lime is needed per 100 g iron. Hence the low content of alumina and high content of lime match the demands for the aluminium slag process [11].

$$2Al_{(diss)} + Fe_2O_{3\,(diss)} = Al_2O_{3\,(diss)} + 2\,Fe_{(l)} \tag{4}$$

CONCLUSIONS

Nickel Ferrite Cermets show promising behavior as an inert oxygen evolving anode in molten calcium chloride. It is found that most of the intergranular copper dissolves within the first 12 hours of the electrolysis. The nickel ferrite cermets should be pre-electrolysed for at least 16 hours.

Graphite anodes dissolve large amounts of carbonate into the electrolyte. The carbonate is further co-reduced at the cathode, when the cathode is run at – 2.0 $V_{AgCl/Ag}$. This is found to halt the reduction of the iron oxide cathode pellet.

Iron oxide particles are found to disperse into molten calcium chloride containing 0.5 mol% calcium oxide. This opens the possibility to run the FFC Cambridge process continuously rather than batch-wise.

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